

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

SPECIFICATION

TITLE OF THE INVENTION

CLAY/ORGANIC CHEMICAL COMPOSITIONS USEFUL AS ADDITIVES TO
POLYMER, PLASTIC AND RESIN MATRICES TO PRODUCE
NANOCOMPOSITES
AND NANOCOMPOSITES CONTAINING SUCH COMPOSITIONS

INVENTORS

MARK ROSS
JACOB KAIZERMAN

PATENT COUNSEL:
MICHAEL J. CRONIN
REGISTRATION NO. 35,848
RHEOX, INC.
WYCKOFFS MILL ROAD
HIGHTSTOWN, NJ 08520
TEL: (609)443-2590
FAX: (609)443-2306

CLAY/ORGANIC CHEMICAL COMPOSITIONS USEFUL AS ADDITIVES TO
POLYMER, PLASTIC AND RESIN MATRICES TO PRODUCE
NANOCOMPOSITES
AND NANOCOMPOSITES CONTAINING SUCH COMPOSITIONS

5

BACKGROUND OF THE INVENTION

Field of the Invention:

The present invention is directed to improved clay/organic chemical compositions that are made from clay and a specified mixture of organic materials. The compositions can be added to a wide variety of polymer, plastic and resin matrices to form inventive nanocomposite materials of enhanced structural strength. They can also be used as rheological additives.

Background of the Invention

Organically modified clays, also called organoclays, have been used for many years as rheological additives for solvent based systems. They are usually produced by making a water dispersion of a phyllosilicate clay, usually a smectite clay, and adding to it a quaternary ammonium salt of a long chain fatty acid to produce an organically modified clay by cation exchange reaction and adsorption. The reaction may cause the organoclay to coagulate from the water dispersion which allows for its isolation by filtration and washing. Similarly, organoclays can be made without water by extrusion mixing, with heat and shear, smectite clay and the quaternary ammonium compound or compounds with no water or other solvent being present. This process usually produces an organoclay of lower quality however, since, among other reasons, the final product still has salt reaction byproducts that cannot be washed or readily isolated from the organoclay and for other reasons.

20

Polymers, resins and plastics containing clay additives have recently become widely used as replacements for heavier steel and other metal products, especially in the field of automotive manufacturing. They have also found use in a growing number of other areas including as bridge components and as replacements for heavier steel parts in ship construction. Using extrusion and injection molding, a nylon matrix, for example, has been successfully reinforced with smectite-type clays (and organoclays based on the smectite clays, bentonite and hectorite) dispersed therein to form molecular composites of nylon and finely dispersed silicate clay platelet layers. Such products, often called nanocomposites, have enhanced structural, tensile, impact and flexural strength.

The behavior of the resultant plastic/clay product (or nanocomposite) is qualitatively different from that exhibited by the plastic, polymer or resin alone and has been attributed by some workers in the field to the confinement of the matrix chains between the clay's millions of microscopic layers. It has long been known that bentonite and hectorite are clays which are composed of flat silicate platelets of a thickness no more than about one nanometer.

The nanocomposite products created to date have important commercial applications not only in the synthesis and properties of organic/inorganic nano-structures as discussed above but also in diverse areas such as where ultrathin polymer films confined between adsorbed surfaces are involved. These uses include polymer composites for polymer adhesives and films including polyethylene.

The clays used are typically smectite clays which are layered phyllosilicates. Smectite clays possess some structural characteristics similar to the more well-known minerals talc and mica. Their crystal structures consist of two-dimensional layers formed by fusing two silica tetrahedral sheets to an edge-shared dioctahedral or trioctahedral sheet of either alumina (for example bentonite) or magnesia (for example hectorite) - each of the different smectite clays having somewhat different

structures. Stacking of these layers in nature in depths of hundreds or more caused by ionic and weak Van der Waals forces leads to voids or chambers between the separate layers. These chambers are occupied by cations which balance the charge deficiency that is generated by isomorphous substitution (often called disharmonies) within the platelet lattices.

5 Nanocomposites are most often prepared today using organically modified silicates or organoclays produced by a cation exchange reaction between the silicate and an alkylammonium salt (usually quaternary ammonium compounds). The alkyl cations exchanged onto the natural clay platelets render the hydrophilic clay organophilic and this transformation makes the clay more easily dispersible into the polymer or plastic. Although excellent sorbents for some organics, natural bentonite and hectorite are themselves very hydrophilic.

Description of the Prior Art:

 The earliest scientific work using organoclays in the preparation of nanocomposites is reflected in U.S. Patent 2,531,396, issued to a predecessor of Rheox, Inc., the assignee of this invention. This patent filed in 1947 teaches the use of organically modified bentonites to provide structural reinforcement to elastomers, such as rubber, polychloroprene and polyvinyl compounds. Over a generation later, additional patents begin to appear. A number of patents obtained by Toyota starting in 1984: U.S. Patent Nos. 4,472,538; 4,739,007; 4,810,734; 4,889,885; and 5,091,462 use organoclay additives for plastics and describe plastic structures commercially used, for example, to replace steel components in automobiles.

20 While not related to nanocomposites, Rheox, Inc. has issued patents describing organoclay compositions useful as rheological additives which comprise the reaction product of smectite clay, quaternary ammonium compounds and organic anions wherein a quaternary-organic anion complex

is intercalated with the smectite clay - see for example U.S. Patent No. 4,412,018 - organic anions are described to include a large variety of organic compounds, including carboxylic acids, capable of reacting with the quaternary used.

Manufacture to date of nanocomposite materials has often involved mixing an organoclay with a polymer powder, pressing the mixture into a pellet, and heating at the appropriate temperature. For example, polystyrene has been intercalated by mixing polystyrene with an alkylammonium montmorillonite and heating in vacuum. Temperature of heating is chosen to be above the bulk glass transition temperature of polystyrene ensuring polymer melt.

Representative U.S. Patent No. 4,810,734 to Toyota describes a different process for producing a composite material which comprises a step of contacting a layered smectite clay mineral having a cation exchange capacity of up to 200 milliequivalents per 100 g with a swelling agent in the presence of a dispersion medium, thereby forming a complex which has the property of being swollen by a molten monomer of a polymer, and a polymerization step of polymerizing said monomer in said mixture. The "swelling agent" used is one which has both an onium ion and a functional group capable of reacting with a polymer. Toyota U.S. Patent No. 4,889,885 describes a composite material, which comprises (a) at least one resin selected from the group consisting of a vinyl-based polymeric compound, a thermosetting resin and a rubber, and (b) a layered bentonite uniformly dispersed in the resin, the layered silicate having a layer thickness of about 7 to 12 Å and an interlayer distance of at least about 30 Å, where at least one resin is connected to a layered silicate through an intermediate.

There are a number of ECC America patents issued starting around 1987 where gaseous NH_3 is used to provide modification of the smectite clay surfaces prior to making a nanocomposite - See

U.S. Patent No. 4,690,868 and 4,798,766.

Two other major companies appear to be working in the field; Amcol International Corporation and AlliedSignal. Both have issued recent patents in the area of this invention. See for example AlliedSignal's U.S. Patent Nos. 5,514,734 and 5,385,776 - these patents are in general directed toward a nylon 6 matrix and clays using non-standard organic modifications. See also in this regard Vaia et al., the article entitled Synthesis and Properties of Two-Dimensional Nano Structures By Direct Intercalation of Polymer Melts in Layered Silicates, Chemical Materials 1993, 5, pages 1694-1696.

Amcol International Corporation (Amcol) has been issued as least three recent patents, U.S. Patent Nos. 5,552,469, 5,578,672 and 5,698,627 which teach the exclusion from their clay-based nanocomposites of "onium ion" products (which would include most known commercial organoclays made with traditional quaternary ammonium compounds). See also Amcol U.S. Patent No. 5,721,306.

Several patents of the Cornell Research Foundation have issued - U.S. Patent No. 5,032,546, 5,032,547 and 5,554,670. One or more of these patents describe the use of organoclays made by the Southern Clay Corporation, Texas.

General Electric Company U.S. Patent No. 5,530,052 describes silicate materials, including montmorillonite clays, modified with at least one heteroaromatic cation and used as additives to specified polymers to make nanocomposites.

Other prior art shows making polymer-clay intercalates directly by reaction of the monomers in the presence of clays. See Interfacial Effects On The Reinforcement Properties Of Polymer Organoclay Nanocomposites, H Shi, T Lan, TH Pinnavaia, Chemistry of Materials, 1996, pages 88

et seq.

Many of the products described in the prior art references described above have the problem that they are either easy to process and isolate, but are difficult to disperse in a matrix, or they have improved dispersing characteristics but are inconvenient to isolate when manufactured. Traditional organoclays manufactured from quaternary salts and smectite clays are easy to isolate and wash because the reaction of onium salts with ion-exchangeable clays form hydrophobic materials in water that can be conveniently filtered. These materials, however, do not have good compatibility with certain plastic materials.

Water soluble polymer-clay intercalates as described in US 5,552,469, for example, can have good compatibility with polymer, resin and plastic materials, but to isolate the additive, one must boil off residual water in an energy intensive fashion. This process also has the potential to leave behind unintercalated polymer along with the clay-polymer intercalate for which there is no simple way of removal. Making a clay-monomer composition with subsequent polymerization can give a well dispersed system in the polymer. Unfortunately, this technique requires that an expensive polymerization train be dedicated to the process and plant contamination with clay can become an issue.

What has escaped scientists is an inexpensive way to make an organic/clay composition that can easily and economically be isolated in high purity and also can be simply processed into a polymer, plastic or resin matrix to form a nanocomposite.

OBJECT AND SUMMARY OF THE INVENTION

Object of the Invention

It is an object of the invention to provide a clay/organic chemical composition (which we also call a hybrid organoclay) that can be readily dispersed in plastic and polymer materials to make nanocomposites of improved structural strength.

It is a specific object of the invention to provide such a clay/organic chemical composition that can be readily made and provide use as a rheological additive.

It is a still further object of the invention to provide an inexpensive process to make the clay/organic chemical composition in a manner that can be isolated readily.

Summary of the Invention:

This invention is of a clay/organic chemical composition that consists of an organic chemical/smectite clay intercalate that has been ion-exchanged and reacted with one or more quaternary ammonium compounds. This composition is designated as a hybrid organoclay. Since such a hybrid organoclay is hydrophobic, it can be washed with water after manufacture to remove reaction salts and excess water soluble or water dispersible organic material to give a clean product via inexpensive means such as filtration. This allows a better dispersing composition to be prepared without the difficulties of isolation presented by prior art, which uses energy intensive means to remove the bulk of the water from the final product and cannot be easily washed.

In one aspect, the present invention provides a clay/organic chemical composition that comprises: (a) one or more smectite clays, (b) one or more quaternary ammonium compounds which react via an ion exchange mechanism with the clay, and (c) one or more defined non-anionic organic materials that are intercalated with the smectite clay.

Further advantages and features of the invention, as well as the scope, nature and utilization of the invention, will become apparent to those of ordinary skill in the art from the description of the preferred embodiment of the invention set forth below.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

5 The clay/organic chemical compositions of this invention, which are also referred to as hybrid organoclays, may be made using a variety of materials and by a variety of methods disclosed hereafter, or which will appear obvious when the disclosure of this patent occurs. Applicants do not intend to limit the materials or methods of manufacture of such additives by the following descriptions.

10 One important aspect of the invention is a clay/organic chemical composition, i.e., a hybrid organoclay, comprising an ion-exchanged reaction product obtained by the intercalation and reaction of:

- 15 a) one or more smectite clays;
- b) one or more quaternary ammonium compounds; and
- c) one or more non-anionic organic materials.

The latter two materials can be reacted and intercalated together, or in any order, with the smectite clay to produce an inventive composition which can be isolated, washed and filtered at low cost.

20 Clays useful for element a) are smectite clays. Such clays are swellable layered clays which contain individual platelets which increase their interlayer spacing upon application of either element b) or c). Useful swellable layered materials include phyllosilicates such as smectite clay minerals, e.g., montmorillonite, particularly sodium montmorillonite; bentonite; hectorite; saponite; stevensite;

beidellite; and the like.

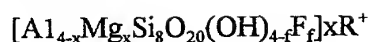
As used herein the term "interlayer spacing" refers to the distance between the internal faces of adjacent dry smectite clay platelet layers as they are assembled in the layered clay before any delamination takes place. The interlayer spacing is measured when the clay is dry; i.e., contains less than 3-6% by weight of water based on the dry weight of the material.

The clays which may be used in the present invention are preferably smectite-type clays having a cationic exchange capacity of at least 50 milliequivalents per 100 grams of clay, 100% active clay basis, as determined by the well-known ammonium acetate or methylene blue methods. Preferred smectite materials are bentonite and hectorite clays particularly of the 2:1 type having a negative charge on the layers ranging from about 0.15 to about 0.9 charges per formula unit and a commensurate number of exchangeable metal cations in the interlayer spaces.

Smectite-type clays are well known in the art and are commercially available from a variety of sources. Prior to use in the invention, the clays may preferably be converted to the sodium form if they are not already in this form. This may be conveniently carried out by preparing an aqueous clay slurry and passing the slurry through a bed of cation exchange resin in the sodium form. Alternatively, the clay can be mixed with water and a soluble sodium compound, such as sodium carbonate, sodium hydroxide, etc., and the mixture sheared, such as with a pugmill or extruder.

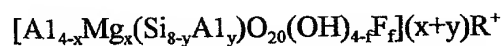
Representative smectite clays useful in accordance with the present invention are the following:

Montmorillonite



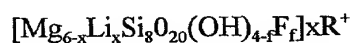
where $0.55 \leq x \leq 1.10$, $f \leq 4$ and R is selected from the group consisting of Na, Li, NH_4 , and mixtures thereof;

5 Bentonite



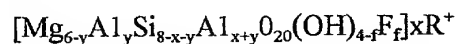
where $0 < x < 1.10$, $0 < y < 1.10$, $0.55 \leq (x + y) \leq 1.10$, $f \leq 4$ and R is selected from the group consisting of Na, Li, NH_4 , and mixtures thereof;

Hectorite



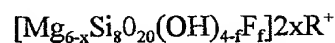
where $0.57 \leq x \leq 1.15$, $f \leq 4$ and R is selected from the group consisting of Na, Li, NH_4 , and mixtures thereof;

Saponite



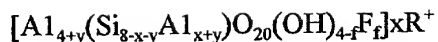
where $0.58 \leq x \leq 1.18$, $0 \leq y \leq 0.66$, $f \leq 4$ and R is selected from the group consisting of Na, Li, NH_4 , and mixtures thereof; and

Stevensite



where $0.28 \leq x \leq 0.57$, $f = 4$ and R is selected from the group consisting of Na, Li, NH_4 , mixtures thereof.

Beidellite

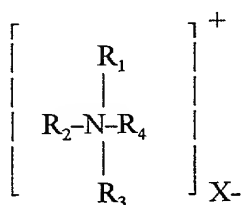


where $0.55 \leq x \leq 1.10$, $0 \leq y \leq 0.44$, $f \leq 4$ and R is selected from the group consisting of Na, Li, NH_4 , and mixtures thereof;

5 The preferred clays used in the present invention are bentonite and hectorite. Bentonite and its properties are described at length in the chapter entitled "Bentonite," in Carr, D., ed. 1994, Industrial Minerals and Rocks, 6th Edition (published by the Society For Mining, Metallurgy and Exploration, Colorado).

It will be understood that both sheared and non-sheared forms of the above-listed smectite clays may be employed. In addition, the smectite clay employed can be either crude (containing gangue or non-clay material) or beneficiated (gangue removed). The ability to use crude clay in the smectite-type clay of this invention represents a substantial cost savings, since the clay beneficiation process and conversion to the sodium form do not have to be carried out.

Compound(s) b) of the invention is a quaternary ammonium compound(s) which include those having the formula:



wherein R_1 comprises a group selected from (i) linear or branched aliphatic, aralkyl, or aromatic hydrocarbon groups having from 8 to 30 carbon atoms or (ii) alkyl or alkyl-ester groups having 8 to 30 carbon atoms; R_2 , R_3 and R_4 are independently selected from the group consisting of (a) linear or

5 branched aliphatic, aralkyl and aromatic hydrocarbon, fluorocarbon or other halocarbon groups having from 1 to about 30 carbon atoms; (b) alkoxyated groups containing from 1 to about 80 moles of alkylene oxide; (c) amide groups, (d) oxazolidine groups, (e) allyl, vinyl, or other alkenyl or alkynyl groups possessing reactive unsaturation and (f) hydrogen; and X^- comprises an anion selected from the group consisting of chloride, methyl sulfate, acetate, iodide and bromide, preferably chloride. For purposes of this invention, quaternary phosphonium and sulfonium based salts are defined as within the definition of quaternary ammonium compound.

The raw materials used to make the quaternary ammonium compounds can be derived from natural oils such as tallow, soya, coconut and palm oil. Useful aliphatic groups in the above formula may be derived from other naturally occurring oils including various vegetable oils, such as corn oil, coconut oil, soybean oil, cottonseed oil, castor oil and the like, as well as various animal oils or fats. The aliphatic groups may likewise be petrochemically derived from, for example, alpha olefins. Representative examples of useful branched, saturated radicals included 12-methylstearyl and 12-ethylstearyl.

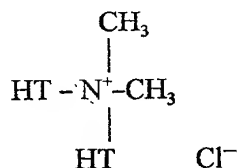
15 Examples of useful aromatic groups, that is benzyl and substituted benzyl moieties, include benzyl and benzylic-type materials derived from benzyl halides, benzhydryl halides, trityl halides, -halo- -phenylalkanes wherein the alkyl chain has from 1 to 30 carbon atoms, such as 1-halo-1-phenyloctadecane; substituted benzyl moieties, such as those derived from *ortho*-, *meta*- and *para*-chlorobenzyl halides, *para*-methoxybenzyl halides, *ortho*-, *meta*- and *para*-nitrilobenzyl halides, and *ortho*-, *meta*- and *para*-alkylbenzyl halides wherein the alkyl chain contains from 1 to 30 carbon atoms; and fused ring benzyl-type moieties, such as those derived from 2-halomethylnaphthalene, 9-halomethylantracene and 9-halomethylphenanthrene, wherein the halo group comprises chloro,

bromo, or any other such group which serves as a leaving group in the nucleophilic attack of the benzyl type moiety such that the nucleophile replaces the leaving group on the benzyl type moiety.

Examples of other aromatic groups include aromatic-type substituents include phenyl and substituted phenyl, N-alkyl and N,N-dialkyl anilines, wherein the alkyl groups contain between 1 and 30 carbon atoms; ortho-, meta- and para-nitrophenyl, ortho-, meta- and para-alkyl phenyl, wherein the alkyl group contains between 1 and 30 carbon atoms, 2-, 3-, and 4-halophenyl wherein the halo group is defined as chloro, bromo, or iodo, and 2-, 3-, and 4-carboxyphenyl and esters thereof, where the alcohol of the ester is derived from an alkyl alcohol, wherein the alkyl group contains between 1 and 30 carbon atoms, aryl such as phenol, or aralkyl such as benzyl alcohols; and fused ring aryl moieties such as naphthalene, anthracene, and phenanthrene.

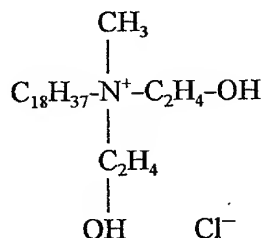
Some examples of preferred quaternary ammonium compounds to make the compositions of this invention are:

Dimethyl dihydrogenated tallow ammonium chloride (2M2HT):

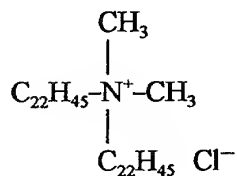


wherein HT = hydrogenated tallow.

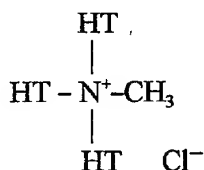
Methyl bis[2-hydroxyethyl] stearyl ammonium chloride (M2HES):



Dimethyl dibehenyl ammonium chloride:



Methyl tris[hydrogenated tallow alkyl] chloride:



A preferred quaternary ammonium compound for purposes of the invention comprises a quaternary ammonium salt that contains at least one, preferably two or three, hydrocarbon chains having from about 8 to about 30 carbon atoms and either no hydrophilic carbon chains or having hydrophilic radicals having a total of about 9 moles of ethylene oxide or less.

It is necessary to have sufficient hydrophobicity in the alkyl chain on the salt to insure that the final product will be non-water dispersible. In general, it is necessary to have at least one of the alkyl chains at least 10 carbon atoms long for this to occur.

The preparation of the quaternary ammonium compounds utilized to make the hybrid organoclay inventive compositions can be carried out by techniques well-known in the art. For example, when preparing a quaternary ammonium salt, one skilled in the art would prepare a dialkyl secondary amine, for example, by the hydrogenation of nitriles (see U.S. Patent No. 2,355,356), and then form the methyl dialkyl tertiary amine by reductive alkylations using formaldehyde as a source of the methyl radical.

Non-anionic organic materials useful for element c) can be selected from a wide variety of non-anionic materials which are either liquids or can be made into a liquid at reaction temperature so that the aforementioned clay materials absorb them. Such absorption is often referred to as intercalation. These materials can be any of a wide range of materials and can have a wide range of molecular weights.

Materials suitable for element (c) of this invention include polyurethanes; polyamides; polyesters; polycarbonates; polyepoxides and polyolefins. Such materials also include polyethers (polymers and copolymers) based on ethylene oxide, butylene oxide, propylene oxide, phenols and bisphenols; polyesters (polymers and copolymers) based on aliphatic and aromatic diols and polyurethanes based on aliphatic and aromatic diisocyanates, polyamides (polymers and copolymers) based on aliphatic and aromatic diamines, and polycarbonates (polymers and copolymers) based on aliphatic or aromatic diols; polycarboimides (polymers and copolymers) based on tetrabasic acids and diamines, vinyl polymers and copolymers based on vinyl monomers, styrene and derivatives of styrene; acrylic polymers and copolymers based on acrylic monomers; copolymers based on styrene, vinyl and acrylic monomers; polyolefin polymers and copolymers based on ethylene, propylene and other alphaolefin monomers; polymers and copolymers based on dienes, isobutylenes and the like; and copolymers based on dienes, styrene, acryl and vinyl monomers. The definition of element c) does not include quaternary ammonium compounds.

Specific preferred examples of useful non-anionic organic materials include THIXATROL VF-10 and THIXATROL VF-20 which are liquid polyester amide copolymers made by RHEOX. Examples of other specific materials are polyvinylpyrrolidone (PVP) or its hydrolysis product, polyvinyl alcohol (PVA), polymethacrylamide, poly(N,N-dimethylacrylamide), poly(N-

isopropylacrylamide), poly(N-acetamidacryl amide), poly(N-acetimidomethacrylamide), polyvinylloxazolidone, and polyvinylmethyl oxazolidone, polyoxypropylene, polyoxyethylene and copolymers thereof.

At least two general methods can be used to make these hybrid organoclays. One is to first
5 disperse the smectite clay in water. The clay is preferably dispersed in water at a concentration of from about 1 to 80%, most preferably from about 2 to 8% by weight. Optionally, the slurry may be centrifuged to remove non-clay impurities which constitute about 10% to 50% of the starting clay composition. The water soluble/dispersible non-anionic organic material is added to the clay/water dispersion and mixed until a clay-organic intercalate is formed. This mixture is then heated and ion exchanged with a quaternary ammonium compound to form the final hybrid organoclay as a coagulate, which is washed with water and isolated by filtration.

The second general method to prepare this invention uses dry clay that is intimately mixed with the non-anionic organic material in a heated device, such as an extruder. The mixture can also have some water present to facilitate intercalation. After the intercalation is complete, the quaternary ammonium compound is added and the final product is produced. This composition can be washed
5 with water and dried.

Both of the methods mentioned above can be modified by either: 1) reversing the order of addition, i.e., react the clay with the quaternary ammonium ion followed by the non-anionic organic material; or 2) adding the quaternary ammonium compound and non-anionic organic material to the
20 clay simultaneously.

The reaction is followed by drying and grinding the organoclay product. Other methods for making this invention can be postulated by those knowledgeable in the art.

5 The preferred amounts and types of clays, organic material and quaternary ammonium compound used to make the compositions of this invention will vary depending upon the type of matrix polymer that each composition is to be mixed into with the goal to achieve substantially complete exfoliation of the clay platelets in the matrix polymer. It is typical that the ratio of component (c) to component (a) clay will be at least 5:100 to 80:100 and more preferably 15:100 to 50:100. The ratio of component (b) to component (a) clay will be determined by the ability to make the final product sufficiently hydrophobic to allow for precipitation and convenient subsequent washing and filtration, as well as good incorporation in the polymer matrix. This will vary depending on the hydrophobicity of the carbon chains attached to the quaternary. Typically, 15 parts of organic cation, more typically 30 to 40 parts per 100 parts of clay are preferred.

A preferred clay/organic chemical composition for purposes of the instant invention comprises the reaction product of:

- (a) a smectite-type clay having a cation exchange capacity of at least 50 milliequivalents per 100 grams of clay; and
- (b) one or more quaternary ammonium compounds in an amount of from about 40% to about 200% of the cation exchange capacity of the smectite-type clay and
- (c) one or more non-anionic organic materials.

The smectite-type clay can be sheared in slurry form prior to reaction with the quaternary ammonium salt, or treated in solid form with a pugmill or similar apparatus.

20 The composition can be used with base materials to make nanocomposites. Such base materials or matrices include almost all plastics, polymers and resins including resins based on formaldehyde and prepolymers thereof and alkyd resins based on dibasic aromatic acids and

anhydrides, glycerol and carboxylic acids, as well as ureas, phenols and melamines. Some of such resins have in the past been used as coatings and have had prior art organoclays dispersed therein.

In addition, polyurethanes of all types produced from isocyanates, polyethers including polyethylene and polypropylene glycols, polyamines, polyamidoamines, polyesters including unsaturated polyesters, plastics based on styrene, vinyl, allyl and acrylic monomers, polyamides, polyolefins and polyimides can be made into nanocomposites by this invention. Polymers also include rubber products including thermoplastic and vulcanizable rubbers.

Preferred matrices are polymeric materials possessing polar functional groups including compounds with hydroxyl, urethane, ester, amide acid, ketone, aldehyde, halide, cyanide and thiol functionality.

Most preferred polymers are plastics which are homopolymers or copolymers of polyesters including linear polyesters, polyamides including nylon and most particularly nylon 6, polyethers, polycarbonates, polyacetal resins and mixtures and blends thereof.

The amount of the clay/chemical compositions of this invention dispersed into the above referenced polymers, resins and plastics to form the inventive nanocomposites varies depending on the particular matrix, its intended use, and the structural strength increase demanded. Preferred amounts are between 1% and 30% by weight of the nanocomposite with a most preferred range being between 3.5% and 12.0%.

For making nanocomposites, the clay/chemical compositions of this invention can be added by any means that can create sufficient shear for mixing. The shear can be provided by any appropriate method such as mechanical, thermal shock, pressure changes or ultrasonics as known in the art. Particularly useful are methods where a flowable polymer is mixed with the hybrid

organoclay by mechanical means such as extruders, roll mills, stirrers, Banbury® type mixers, Brabender® type mixers and continuous mixers.

Nanocomposites that are made by these methods using the compositions of this invention will typically exhibit improved tensile modulus, tensile strength, gas barrier and heat distortion temperature values when sufficient energy is imparted to the blend to create substantially intercalated or exfoliated mixtures.

The clay/organic chemical compositions of this invention can also be used as rheological additives for liquid organic systems, such as paints and coatings, to provide viscosity modification and flow and leveling properties to such systems.

The following examples are given to illustrate the invention, but are not deemed to be limiting thereof. All percentages and ratios given throughout the specification are based upon weight, 100% weight basis, unless otherwise indicated.

Example I

In a baffled three liter reactor with efficient stirring was placed 1350g of a prehydrated aqueous hectorite clay slurry (concentration of clay = 2.8%). The mixture was heated to 70-80° C with stirring. Non-anionic organic materials, as shown below, at a level of 30% based on calculated clay weight were added to the slurry and stirred 15 minutes to effect intercalation. Sufficient alkyl quaternary ammonium compounds in 60 mL of isopropanol were added to react with 100% of the measured cation exchange capacity of the clay and the solution mixed at temperature for an additional 45 minutes.

The initial process used was addition of the non-anionic organic material to the clay slurry quickly as a single shot (Method 1) . It was found that, in some cases, absorption was so rapid as to

cause some clay to not have maximum possible intercalation. Where this was evident by X-Ray diffraction, new hybrid organoclays were prepared using a second method of manufacture (Method 2). This method was addition of the non-anionic organic material slowly to the clay slurry.

The precipitated product was filtered on a large Büchner funnel and redispersed in 1 L of water at 70° C to wash the hybrid clay. The final product was refiltered, dried at 65° C in an oven to give a moisture content below 0.5% and ground to less than 325 mesh. A number of examples are shown in Table 1 showing the d_{001} spacing measured using state of the art X-Ray diffraction measurement equipment.

TABLE 1
Hybrid Organoclays Prepared and Their Properties

Run #	Clay	Non-Anionic Organic Material ⁴	Commercial Name	Quaternary	Method	d ₀₀₁ (Å)	Δd ₀₀₁ (Å) ¹
1	Hectorite	p(vinylpyrrolidone/AA)	ACP-1005 ⁵	M2HES ³	A	22.86	+4.49
2	Hectorite	p(vinylmethylether/MA)	Gantrez AN119 ⁵	M2HES	A	22.86	+4.49
3	Hectorite	p(vinylmethylether/MA)	Gantrez AN179 ⁵	M2HES	A	21.14	+2.77
4	Hectorite	p(vinyl formal)	50,000 MW	M2HES	A	29.47	+11.10
5	Hectorite	p(ethylene oxide)	ca. 100,000 MW	M2HES	A	27.48	+9.11
6	Hectorite	p(vinyl alcohol)	Airvol 523 ⁶	M2HES	A	26.20	+7.83
7	Hectorite	p(ethylene glycol)	8220 MW	M2HES	A	21.97	+3.60
8A	Hectorite	polyamide	THIXATROL VF-10 ⁷	2M2HT	A	36.11	+10.65
8B	Hectorite	polyamide	THIXATROL VF-10 ⁷	2M2HT	B	40.0	+14.5
9	Hectorite	polyurethane	RHEOLATE 204 ⁷	2M2HT	A	33.92	+8.47
10	Hectorite	p(styrene/MA)	SMA 3000 ⁸	2M2HT	A	28.71	+3.29
11	Hectorite	p(dimethylsiloxane)	Antifoam 1400 ⁹	M2HES	A	19.32	+0.95
12	Hectorite	p(dimethylsiloxane)	Antifoam B ⁹	M2HES	A	19.66	+1.29
13	Hectorite	polyacrylamide	10,000 MW	2M2HT	A	31.10	+12.73
14	Hectorite	polyester amide	E1075/ADA/AEPD	M2HES	A	40.69	+22.60
15A	Hectorite	polyamide	THIXATROL VF-20 ⁷	M2HES	A	43.88	+25.51
15B	Hectorite	polyamide	THIXATROL VF-20 ⁷	M2HES	B	40.0	+21.6
16	Hectorite	polyamide	Jef2000/E1004/NMG	M2HES	A	36.11	+17.74
17A	Hectorite	polyester	C15/E1004/E1040	M2HES	A	41.45	+23.08
17B	Hectorite	polyester	C15/E1004/E1040	M2HES	B	40.0	+21.6
18	Hectorite	polyamide	EDA/HSA/E1040	M2HES	A	20.01	+1.637
19	Hectorite	polyamide	EDA/E1004/NMG	M2HES	A	34.71	+16.34
20A	Hectorite	polyester amide	C15/E1004/NMG	M2HES	A	38.59	+20.22
20B	Hectorite	polyester amide	C15/E1004/NMG	M2HES	B	40.0	+21.6
21	Hectorite	polyester amide	C15/E1004/NMG	2M2HT	B	40.0	+14.5
22	Bentonite	p(ethylene oxide)	600,000 MW	M2HES	B	24.9	+4.5
23	Bentonite	polyamide	THIXATROL VF-10 ⁷	M2HES	B	38.6	+20.2
24	Bentonite	polyester amide	C15/E1004/NMG	M2HES	B	44.8	+24.4

¹ Difference in d_{001} spacing from control organoclay, i.e. organoclay made solely with a quaternary compound

² 2M2HT = Dimethyldihydrogenated tallow ammonium chloride.

³ M2HES = Methyl bis[(2-hydroxyethyl)]stearyl ammonium chloride.

⁴ Monomers: Empol (Emory) 1075 - dimer diol, Empol 1004 -dimer acid, Empol 1040- trimer acid, ADA-adipic acid, AEPD-aminoethylpropanediol, AA-acrylic acid, MA-maleic anhydride, Jef2000-Jeffamine D2000 (Huntsman)-diamine, NMG-N-methylglucamine, C15- Ethomeen C15 (Akzo) alkylaminopolyetherol, EDA-ethylenediamine, HSA-hydroxystearic acid.

⁵ International Specialty Products (ISP).

⁶ Air Products

⁷ RHEOX commercial product

⁸ ElfAtochem

⁹ Dow Corning

Description of Results:

Table 1 examples show that a variety of clay/organic chemical compositions cause increased d_{001} spacing in the system tested and that the use of a non-anionic organic material plus a quaternary compound caused an increase in spacing over and above that caused by the quaternary alone (Δd_{001} column).

Example 2

Some of the compositions from Example 1 were selected at random and further tested to determine their ability to disperse in a thermoplastic polymer. PETG, a glycol modified polyester from Eastman Chemical, was used. The polyester was melted and worked on a roll mill at 350°F for 2 minutes to form a melt and an amount of the compositions indicated on Table II was added to the polyester. The dispersion results obtained are indicated in Table II.

Table II
Hybrid Organoclay Dispersion in PETG

Sample	Non-Anionic Organic Material	Method ¹	Hybrid Organoclay Loading ²	Dispersion ³
5	p(ethylene oxide)	A	7.79%	Good
7	p(ethylene glycol) 8K MW	A	7.16%	Very Good
8A	THIXATROL VF-10	A	7.90%	Excellent
8B	THIXATROL VF-10	B	7.62%	Excellent
12	p(dimethylsiloxane)	A	7.16%	Good
13	polyacrylamide	A	7.90%	Poor
14	E1075/ADA/AEPD	A	7.16%	Fair
15A	THIXATROL VF-20	A	7.16%	Fair
15B	THIXATROL VF-20	B	7.03%	Very Good
17A	C15/E1004/E1040	A	7.16%	Good
17B	C15/E1004/E1040	B	7.03%	Very Good
18	EDA/HSA/E1040	A	7.16%	Fair
19	EDA/E1004/NMG	A	7.16%	Very Good
20A	C15/E1004/NMG	A	7.16%	Excellent
20B	C15/E1004/NMG	B	7.03%	Excellent
22	p(ethylene oxide) 600,000 MW	B	7.08%	Very Good

¹ Refers to method employed for the preparation of the hybrid organoclay.

² Hybrid organoclay loading as a percentage of polymer weight.

³ Dispersion is evaluated on a 1-5 scale from poor to excellent as measured by visual inspection and SEM/X-Ray microprobe. A rating of poor corresponds to a sample containing large clay segregates with no dispersed material, and excellent corresponds to a sample that contains no segregates and has clay material evenly dispersed throughout the polymer matrix.

Description of Results:

It is clear that a wide variety of hybrid organoclay compositions prepared according to this invention gave varying satisfactory degrees of dispersion by both visual inspection and SEM/X-Ray probe measurements.

Example 3

Several materials were prepared to compare with the hybrid organoclays the dispersibility in PETG resin of 1) traditional organoclays without intercalated polymer, and 2) clays containing intercalated polymer and no quaternary salt. The former materials were prepared as described in U.S. Patent No. 4,105,578, and the latter by the procedure set forth below:

In a baffled three liter reactor with efficient stirring was placed 1350g of a prehydrated aqueous hectorite or bentonite clay slurry (concentration of clay ca. 3.0%). The slurry was heated to 70-80°C with stirring and organic materials as shown below, at a level of 30% based on calculated clay weight, were added to the slurry. The mixture was then mixed at temperature for an additional 45 minutes and poured into a large stainless steel pan. The materials were oven dried at 65°C, followed by mastication, grinding, and sifting to provide a final product less than 325 mesh.

The materials were incorporated into PETG resin as described in Example 2 and their dispersion observed by visual inspection and SEM/X-Ray microprobe analysis. The results are indicated in Table III.

Table III
Comparative Dispersions

Run #	Clay	Non-Anionic Organic Material	Commercial Name	Quaternary	Dispersion ¹
1	Hectorite	---	---	2M2HT	Poor
2	Hectorite	---	---	M2HES	Poor
3	Bentonite	---	---	M2HES	Fair
4	Hectorite	polyester amine	C15/E1004/NMG	---	Poor
5	Hectorite	p(vinyl alcohol)	Airvol 523	---	Poor
6	Bentonite	polyamide	THIXATROL VF-10 ²	---	Poor
7	Bentonite	p(ethylene glycol)	20,000 MW	---	Poor

¹ Dispersion ranked on a 1-5 scale (Poor, Fair, Good, Very Good, Excellent) by visual inspection and SEM/X-Ray microprobe.

² Rheox commercial product

Description of Results:

5 The examples of Table III demonstrate that neither traditional organically modified clays nor non-quaternized clay intercalates dispersed as well in a polymer matrix as the inventive compositions.

Example 4

10 The hybrid organoclay designated sample 21B (Example 1) was tested against a standard organoclay product, BENTONE 38, for efficiency as a rheological additive in coatings. The two materials were incorporated into a standard aromatic gloss alkyd enamel at 1.00% and their Brookfield and Stormer viscosities measured. The results are shown in Table IV.

Table IV
Hybrid Organoclay 21B vs. BENTONE 38¹ in Solvent Based Paint

Material/Incorp. Method	Stormer Visc. (77°F, KU)	Brookfield Visc. (10 rpm, cP)
Blank	74	550
BENTONE 38/Dry Incorporation	88	3040
BENTONE 38/Xylene pregel	90	3400
Sample 21B/Dry Incorporation	84	1760
Sample 21B /Xylene pregel	89	2400

¹ Rheox commercial product.

Description of Results:

While not as efficient as a standard organoclay in this particular example, Sample 21B provided enhanced viscosity to the enamel well within the effective range for rheological additives.

11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
107
108
109
110
111
112
113
114
115
116
117
118
119
120
121
122
123
124
125
126
127
128
129
130
131
132
133
134
135
136
137
138
139
140
141
142
143
144
145
146
147
148
149
150
151
152
153
154
155
156
157
158
159
160
161
162
163
164
165
166
167
168
169
170
171
172
173
174
175
176
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192
193
194
195
196
197
198
199
200
201
202
203
204
205
206
207
208
209
210
211
212
213
214
215
216
217
218
219
220
221
222
223
224
225
226
227
228
229
230
231
232
233
234
235
236
237
238
239
240
241
242
243
244
245
246
247
248
249
250
251
252
253
254
255
256
257
258
259
260
261
262
263
264
265
266
267
268
269
270
271
272
273
274
275
276
277
278
279
280
281
282
283
284
285
286
287
288
289
290
291
292
293
294
295
296
297
298
299
300
301
302
303
304
305
306
307
308
309
310
311
312
313
314
315
316
317
318
319
320
321
322
323
324
325
326
327
328
329
330
331
332
333
334
335
336
337
338
339
340
341
342
343
344
345
346
347
348
349
350
351
352
353
354
355
356
357
358
359
360
361
362
363
364
365
366
367
368
369
370
371
372
373
374
375
376
377
378
379
380
381
382
383
384
385
386
387
388
389
390
391
392
393
394
395
396
397
398
399
400
401
402
403
404
405
406
407
408
409
410
411
412
413
414
415
416
417
418
419
420
421
422
423
424
425
426
427
428
429
430
431
432
433
434
435
436
437
438
439
440
441
442
443
444
445
446
447
448
449
450
451
452
453
454
455
456
457
458
459
460
461
462
463
464
465
466
467
468
469
470
471
472
473
474
475
476
477
478
479
480
481
482
483
484
485
486
487
488
489
490
491
492
493
494
495
496
497
498
499
500
501
502
503
504
505
506
507
508
509
510
511
512
513
514
515
516
517
518
519
520
521
522
523
524
525
526
527
528
529
530
531
532
533
534
535
536
537
538
539
540
541
542
543
544
545
546
547
548
549
550
551
552
553
554
555
556
557
558
559
560
561
562
563
564
565
566
567
568
569
570
571
572
573
574
575
576
577
578
579
580
581
582
583
584
585
586
587
588
589
590
591
592
593
594
595
596
597
598
599
600
601
602
603
604
605
606
607
608
609
610
611
612
613
614
615
616
617
618
619
620
621
622
623
624
625
626
627
628
629
630
631
632
633
634
635
636
637
638
639
640
641
642
643
644
645
646
647
648
649
650
651
652
653
654
655
656
657
658
659
660
661
662
663
664
665
666
667
668
669
670
671
672
673
674
675
676
677
678
679
680
681
682
683
684
685
686
687
688
689
690
691
692
693
694
695
696
697
698
699
700
701
702
703
704
705
706
707
708
709
710
711
712
713
714
715
716
717
718
719
720
721
722
723
724
725
726
727
728
729
730
731
732
733
734
735
736
737
738
739
740
741
742
743
744
745
746
747
748
749
750
751
752
753
754
755
756
757
758
759
760
761
762
763
764
765
766
767
768
769
770
771
772
773
774
775
776
777
778
779
780
781
782
783
784
785
786
787
788
789
790
791
792
793
794
795
796
797
798
799
800
801
802
803
804
805
806
807
808
809
810
811
812
813
814
815
816
817
818
819
820
821
822
823
824
825
826
827
828
829
830
831
832
833
834
835
836
837
838
839
840
841
842
843
844
845
846
847
848
849
850
851
852
853
854
855
856
857
858
859
860
861
862
863
864
865
866
867
868
869
870
871
872
873
874
875
876
877
878
879
880
881
882
883
884
885
886
887
888
889
890
891
892
893
894
895
896
897
898
899
900
901
902
903
904
905
906
907
908
909
910
911
912
913
914
915
916
917
918
919
920
921
922
923
924
925
926
927
928
929
930
931
932
933
934
935
936
937
938
939
940
941
942
943
944
945
946
947
948
949
950
951
952
953
954
955
956
957
958
959
960
961
962
963
964
965
966
967
968
969
970
971
972
973
974
975
976
977
978
979
980
981
982
983
984
985
986
987
988
989
990
991
992
993
994
995
996
997
998
999
1000
1001
1002
1003
1004
1005
1006
1007
1008
1009
1010
1011
1012
1013
1014
1015
1016
1017
1018
1019
1020
1021
1022
1023
1024
1025
1026
1027
1028
1029
1030
1031
1032
1033
1034
1035
1036
1037
1038
1039
1040
1041
1042
1043
1044
1045
1046
1047
1048
1049
1050
1051
1052
1053
1054
1055
1056
1057
1058
1059
1060
1061
1062
1063
1064
1065
1066
1067
1068
1069
1070
1071
1072
1073
1074
1075
1076
1077
1078
1079
1080
1081
1082
1083
1084
1085
1086
1087
1088
1089
1090
1091
1092
1093
1094
1095
1096
1097
1098
1099
1100
1101
1102
1103
1104
1105
1106
1107
1108
1109
1110
1111
1112
1113
1114
1115
1116
1117
1118
1119
1120
1121
1122
1123
1124
1125
1126
1127
1128
1129
1130
1131
1132
1133
1134
1135
1136
1137
1138
1139
1140
1141
1142
1143
1144
1145
1146
1147
1148
1149
1150
1151
1152
1153
1154
1155
1156
1157
1158
1159
1160
1161
1162
1163
1164
1165
1166
1167
1168
1169
1170
1171
1172
1173
1174
1175
1176
1177
1178
1179
1180
1181
1182
1183
1184
1185
1186
1187
1188
1189
1190
1191
1192
1193
1194
1195
1196
1197
1198
1199
1200
1201
1202
1203
1204
1205
1206
1207
1208
1209
1210
1211
1212
1213
1214
1215
1216
1217
1218
1219
1220
1221
1222
1223
1224
1225
1226
1227
1228
1229
1230
1231
1232
1233
1234
1235
1236
1237
1238
1239
1240
1241
1242
1243
1244
1245
1246
1247
1248
1249
1250
1251
1252
1253
1254
1255
1256
1257
1258
1259
1260
1261
1262
1263
1264
1265
1266
1267
1268
1269
1270
1271
1272
1273
1274
1275
1276
1277
1278
1279
1280
1281
1282
1283
1284
1285
1286
1287
1288
1289
1290
1291
1292
1293
1294
1295
1296
1297
1298
1299
1300
1301
1302
1303
1304
1305
1306
1307
1308
1309
1310
1311
1312
1313
1314
1315
1316
1317
1318
1319
1320
1321
1322
1323
1324
1325
1326
1327
1328
1329
1330
1331
1332
1333
1334
1335
1336
1337
1338
1339
1340
1341
1342
1343
1344
1345
1346
1347
1348
1349
1350
1351
1352
1353
1354
1355
1356
1357
1358
1359
1360
1361
1362
1363
1364
1365
1366
1367
1368
1369
1370
1371
1372
1373
1374
1375
1376
1377
1378
1379
1380
1381
1382
1383
1384
1385
1386
1387
1388
1389
1390
1391
1392
1393
1394
1395
1396
1397
1398
1399
1400
1401
1402
1403
1404
1405
1406
1407
1408
1409
1410
1411
1412
1413
1414
1415
1416
1417
1418
1419
1420
1421
1422
1423
1424
1425
1426
1427
1428
1429
1430
1431
1432
1433
1434
1435
1436
1437
1438
1439
1440
1441
1442
1443
1444
1445
1446
1447
1448
1449
1450
1451
1452
1453
1454
1455
1456
1457
1458
1459
1460
1461
1462
1463
1464
1465
1466
1467
1468
1469
1470
1471
1472
1473
1474
1475
1476
1477
1478
1479
1480
1481
1482
1483
1484
1485
1486
1487
1488
1489
1490
1491
1492
1493
1494
1495
1496
1497
1498
1499
1500
1501
1502
1503
1504
1505
1506
1507
1508
1509
1510
1511
1512
1513
1514
1515
1516
1517
1518
1519
1520
1521
1522
1523
1524
1525
1526
1527
1528
1529
1530
1531
1532
1533
1534
1535
1536
1537
1538
1539
1540
1541
1542
1543
1544
1545
1546
1547
1548
1549
1550
1551
1552
1553
1554
1555
1556
1557
1558
1559
1560
1561
1562
1563
1564
1565
1566
1567
1568
1569
1570
1571
1572
1573
1574
1575
1576
1577
1578
1579
1580
1581
1582
1583
1584
1585
1586
1587
1588
1589
1590
1591
1592
1593
1594
1595
1596
1597
1598
1599
1600
1601
1602
1603
1604
1605
1606
1607
1608
1609
1610
1611
1612
1613
1614
1615
1616
1617
1618
1619
1620
1621
1622
1623
1624
1625
1626
1627
1628
1629
1630
1631
1632
1633
1634
1635
1636
1637
1638
1639
1640
1641
1642
1643
1644
1645
1646
1647
1648
1649
1650
1651
1652
1653
1654
1655
1656
1657
1658
1659
1660
1661
1662
1663
1664
1665
1666
1667
1668
1669
1670
1671
1672
1673
1674
1675
1676
1677
1678
1679
1680
1681
1682
1683
1684
1685
1686
1687
1688
1689
1690
1691
1692
1693
1694
1695
1696
1697
1698
1699
1700
1701
1702
1703
1704
1705
1706
1707
1708
1709
1710
1711
1712
1713
1714
1715
1716
1717
1718
1719
1720
1721
1722
1723
1724
1725
1726
1727
1728
1729
1730
1731
1732
1733
1734
1735
1736
1737
1738
1739
1740
1741
1742
1743
1744
1745
1746
1747
1748
1749
1750
1751
1752
1753
1754
1755
1756
1757
1758
1759
1760
1761
1762
1763
1764
1765
1766
1767
1768
1769
1770
1771
1772
1773
1774
1775
1776
1777
1778
1779
1780
1781
1782
1783
1784
1785
1786
1787
1788
1789
1790
1791
1792
1793
1794
1795
1796
1797
1798
1799
1800
1801
1802
1803
1804
1805
1806
1807
1808
1809
1810
1811
1812
1813
1814
1815
1816
1817
1818
1819
1820
1821
1822
1823
1824
1825
1826
1827
1828
1829
1830
1831
1832
1833
1834
1835
1836
1837
1838
1839
1840
1841
1842
1843
1844
1845
1846
1847
1848
1849
1850
1851
1852
1853
1854
1855
1856
1857
1858
1859
1860
1861
1862
1863
1864
1865
1866
1867
1868
1869
1870
1871
1872
1873
1874
1875
1876
1877
1878
1879
1880
1881
1882
1883
1884
1885
1886
1887
1888
1889
1890
1891
1892
1893
1894
1895
1896
1897
1898
1899
1900
1901
1902
1903
1904
1905
1906
1907
1908
1909
1910
1911
1912
1913
1914
1915
1916
1917
1918
1919
1920
1921
1922
1923
1924
1925
1926
1927
1928
1929
1930
1931
1932
1933
1934
1935
1936
1937
1938
1939
1940
1941
1942
1943
1944
1945
1946
1947
1948
1949
1950
1951
1952
1953
1954
1955
1956
1957
1958
1959
1960
1961
1962
1963
1964
1965
1966
1967
1968
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
1984
1985
1986
1987
1988
1989
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011
2012
2013
2014
2015
2016
2017
2018
2019
2020
2021
2022
2023
2024
2025
2026
2027
2028
2029
2030
2031
2032
2033
2034
2035
2036
2037
2038
2039
2040
2041
2042
2043
2044
2045
2046
2047
2048
2049
2050
2051
2052
2053
2054
2055
2056
2057
2058
2059
2060
2061
2062
2063
2064
2065
2066
2067
2068
2069
2070
2071
2072
2073
2074
2075
2076
2077
2078
2079
2080
2081
2082
2083
2084
2085
2086
2087
2088
2089
2090
2091
2092
2093
2094
2095
2096
2097
2098
2099
2100
2101
2102
2103
2104
2105
2106
2107
2108
2109
2110
2111
2112
2113
2114
2115
2116
2117
2118
2119
2120
2121
2122
2123
2124
2125
2126
2127
2128
2129
2130
2131
2132
2133
2134
2135
2136
2137
2138
2139
2140
2141
2142
2143
2144
2145
2146
2147
2148
2149
2150
2151
2152
2153
2154
2155
2156
2157
2158
2159
2160
2161
2162
2163
2164
2165
2166
2167
2168
2169
2170
2171
2172
2173
2174
2175
2176
2177
2178
2179
2180
2181
2182
2183
2184
2185
2186
2187
2188
2189
2190
2191
2192
2193
2194
2195
2196
2197
2198
2199
2200
2201
2202
2203
2204
2205
2206
2207
2208
2209
2210
2211
2212
2213
2214
2215
2216
2217
2218
2219
2220
2221
2222
2223
2224
2225
2226
2227
2228
2229
2230
2231
223